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## (54) THERMOPLASTIC RESIN COMPOSITIONS


(71) We, POLYPLASTICS COMPANY LIMITED, a Japanese Company of 30, 2-chome Azuchimachi, Higashi-ku, Osaka-shi, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-


This invention relates to thermoplastic resin compositions useful as molding materials which have small rates of heat deformation and high strength.

Although thermoplastic resins have been used per se for producing various molded articles, they have also been used as compositions containing reinforcing materials such as glass fibers in such applications as the production of substrate plates, which will require higher rigidity and strength.

Further, for the purpose of imparting and improving the electroconductivity and incombustibility of thermoplastic resins, the addition of fibers, particles, etc. has also been conducted.

However, compositions which contain fibrous additives have a larger anisotropy in general, resulting in the deformation of molded articles during the molding or annealing thereof. Although such deformation is a common phenomenon to be seen in thermoplastic resins, this phenomenon is particularly remarkable in such resins having a high crystallization during the molding as polyacetal and polybutylene terephthalate, and also in such resins whose crystallization is advanced by annealing as polyethylene terephthalate.

These resins are subject to a considerable deformation even per se. Accordingly, their adaptability as molding materials should be determined with an emphasis on the balance between their deformation properties and their rigidity and strength properties, as well as their chemical and thermal properties.

The balance between deformation and physical properties is important particularly in producing such materials as substrate plates and boxes. Looking at the conventionally employed raw materials from this standpoint, virgin resins, though their deformation is relatively small, are inferior in rigidity, and compositions containing particles are small in strength, though their deformation is relatively; small; and, on the contrary, compositions containing fibrous materials are relatively large in deformation, although their strength and rigidity are high. It is therefore very difficult to improve rigidity and other physical properties without deteriorating deformation, and, particularly, there are now no available satisfactory compositions for crystalline resins.

The inventors have investigated the phenomenon of deformation of thermoplastic resins and discovered that compositions which contain fibrous reinforcing materials and platelet fillers in combination are high in physical strength and are subject only to small deformation.

The balance of deformation and strength is an important criterion for all resins and thus the compositions according to this invention are useful regardless of types of the base resin. Although polyacetals, polybutylene terephthalate, polyethylene terephthalate and polyamides are optimum to be used as precision functional components owing to their chemical, thermal, and frictional properties, molding materials containing these resins as base resins are subject to significant deformation during molding or annealing and thus improved grades of such resin compositions have been desired; under such circumstances, this invention will bring about large economical effects particularly when these resins are employed as base resins.

The thermoplastic resin compositions according to the present invention, employing these

resins as base resins, are, particularly in a composition range which will show a relatively small amount of deformation, subject to a smaller absolute amount of deformation even if compared with non-filled or particle filled ones, the latter of which have been said to show the smallest deformation, as well as compared to the conventional fiber-reinforced compositions.

Needless to say, such compositions according to this invention have a higher strength than that of particle filled compositions and remarkably better in the balance of the both qualities, i.e., deformation and strength.

The thermoplastic resin compositions according to this invention are thermoplastic resin compositions characterized by incorporating therein based on the total weight of the composition 1 to 50 weight percent fibrous additives and 5 to 59 weight percent platelet fillers in a range where the whole amount of the both does not exceed 60 weight percent of the total composition.

Fibrous additives to be used in this invention include glass fibers, carbon fibers, graphite fibers, metal fibers, silicon carbide fibers, mineral fibers e.g. asbestos and wollastonite, and organic fiber materials. These additives are used for such various purposes as increasing physical strength, imparting electroconductivity, improving frictional properties, and improving flame resistance. When such fibrous additive is used alone, the length/diameter ratio thereof should be preferably small in order to make the deformation of the resin composition small; e.g. in the case of glass fibers of about 10 micron diameter, the deformation of a resin composition containing 20 to 50 percent (by weight) of a fibrous additive having a length of 100 to 200 microns alone will be relatively small. However, in the resin compositions according to this invention, longer fibers are preferable and, for example, in the case of glass fibers of about 10 micron diameter, the glass fibers having a length of 300 to 600 microns will be preferable.

However, an excessive length of fibers in the compositions will remarkably deteriorate the moldability of the resin composition, and therefore a fiber length of less than one millimeter is desirable.

The platelet fillers to be used in this invention are preferably dry-crushed mica and glass platelets having a diameter of tens to hundreds of microns, but platelet minerals such as sericite having a diameter of several to tens of microns may be employed. Those having a smaller diameter or a smaller diameter/thickness ratio will not be as effective as platelet fillers and may deteriorate the moldability of the resin composition excessively. Talc, kaolinite, bilofilite, and metal foils may also be used as platelet fillers.

Although the addition of such platelet additives will improve electrical and frictional properties of the resin composition and will be more effective against the deformation of the molded products than the addition of particles (for this purpose, the addition of 1 to 60 percent by weight, particularly 30 to 50 percent is preferable), the combination of platelet fillers with fibrous materials according to this invention is much more effective.

Fibrous additives in the compositions according to this invention bring about unexpected unique effects as explained below as well as the improvement of rigidity and strength of the molded products.

Thus the deformation of the molded product when a fibrous material alone is added will be substantial at a low density of less than 10 weight percent and rather small at a high density of 30 to 40 weight percent as the fibrous additive content. However, when a fibrous material and a platelet filler are used together according to this invention, the deformation of the molded product will be smallest at a low density of 2 to 20 weight percent, particularly 3 to 10 weight percent, as the fibrous material content. In the case of crystalline resins, it is small even compared to the case when particle fillers are used.

Accordingly, the addition of 2 to 20 weight percent, particularly 3 to 10 weight percent of the fibrous additive will be preferable. However when rigidity should be especially emphasized or in the case electroconductivity is required, a higher density of the fibrous additive may be used; even in this case, the deformation of the molded product will be small compared to the case where a fibrous additive is used alone or it is used with an additive in the form of particles.

As mentioned above, a platelet filler used in this invention exhibits its unique deformation reduction effect owing to its synergistic action with a fibrous additive and a smaller reduction of strength compared with a particle-like additive.

The more platelet filler is added the larger is its deformation preventing effect, and, as the reduction of strength of the moulded product is relatively small, the amount used should be preferably large. However an excessive amount affects the mouldability of the resin composition. About 60 weight percent of the platelet filler is practically the upper limit of the total amount of the platelet filler with the fibrous reinforcing material. About 30 to 50 weight percent of the total amount of the additives is preferable. When a lower elasticity of the moulded product is preferable, lower densities of the additives may be used.

A particulate additive may also be included in the compositions of the invention in a range

where the mouldability of the resin composition is not remarakbly deteriorated. Such particulate additives include magnesium hydroxide, calcium sulphide, clay, diatomaceous earth, alumina glass beads, calcium hydroxide, quartz powder, siliceous sand, glass powder, metal powder, antimony trioxide, graphite, organic macromolecules e.g. fluorine resins, and organic crystalline material e.g, brominated diphenyl. The particulate additives may be used for the purpose of reducing the amount of platelet fillers to be used. Further, they can be used for the purpose of improving the electroconductivity, flame retardance, and frictional properties of the molded product, which are characteristic of such particle additives. Those various additives may be used without any pretreatment or with a surface treatment by use of compounds of for example silane or titanium.

These treatments are useful for improving physical properties and fluidity of the resin composition. Base resins and the above various kinds of additives may be of one type respectively or two or more types thereof may be used together.

The compositions according to this invention may contain other ingredients such as antistatic agents, coloring agents, lubricants, stabilizers and flame retarders.

The thermoplastic resin compositions according to this invention may be easily prepared by the methods which have been usually employed for the preparation of reinforced plastic resins and filler-incorporated resins.

For example, respective additives can be mixed with the base resin by means of an extruding machine to produce resin pellets having the composition according to this invention, which can then be molded. (In this case, the fibrous additive may be used in a bundled or non-bundled state or as long or short fibers.) Further, pellets having different compositions can be mixed in molding, or respective components can be directly charged into a molding machine.

The effects of this invention will be shown below by employing polybutylene terephthalate, which is particularly suitable to the present invention, as an example.

The invention is hereinafter particularly described and illustrated by the accompanying drawings, and the Examples.

The accompanying drawings show the test pieces used in the Examples and Comparative Examples. Figure 1 is a plan view and Figure 2 is a cross-sectional view.

Examples 1 to 10

The resin mixtures containing the additives having the compositions as described in Table-1, respectively, which comprise polybutylene terephthalate as the base resin were extruded through an extruding machine of 300 mm diameter to produce pellets. The glass fiber was used as bundled fibers of 6 mm length.

From these pellets, plate test pieces as shown in Figures 1 and 2 were molded, the test pieces containing a projection, depression and holes to simulate practical mouldings. The difference between the highest part and the lowest part in the test piece was measured, which was taken as the amount of deformation. Further, the load at break was measured by supporting the circumference of the test piece and compressing the center part thereof, which was taken as strength.

The ratio of the both was calculated, taking it as a measure of balance between deformation and strength. The results are shown in Table-1.

Explanation of the symbols shown in Figures 1 and 2 and the dimensions of the test piece are shown below:

| | | |
|---|---|---|
| X : | lateral width of test plate | 50 (unit: mm, the following are the same) |
| Y : | longitudinal width of test plate | 45 |
| t : | thickness of test plate | 2 |
| l : | moulding gate | pin of 1.5 mm diameter |

(The following parts are indicated by their co-ordinates, of which the original point is the moulding gate 1.)

2 : projection on the plate surface, the co-ordinates of the center thereof (2.25 mm, 2 mm), diameter 3 mm, height 2.5 mm

3 : hole, the co-ordinates of the center thereof (0, 1.25), diameter 5 mm

4 : hole, the co-ordinates of the center thereof (-1.5, 1.25), diameter 5 mm

5 : hole, the co-ordinates of the center thereof (0, -1.5), diameter 8 mm

6 : circular depression on the plate surface, the co-ordinates of the center thereof (1.5, -1), diameter 15 mm, depth 1 mm

Comparative Examples 1 to 10

The deformation and strength were measured in the same manner as shown in the Examples on various resin compositions to be compared with those compositions according to the present invention as exemplified in Examples 1 to 10. The results are shown in Table 2.

The comparison of the two tables indicates that the compositions according to the present invention are good materials having larger ratios of strength/deformation than those of the Comparative Examples. Further, the absolute amounts of deformation are smaller, in the optimum composition of the Examples, compared to the Comparative Examples.

*Table 1*

| Examples | Compositions (% by weight): Glass Fiber (1) | Mica (3) | Glass Bead (4) | Calcium Hydroxide (5) | Strength (Kg) | Deformation (mm) | Ratio of Strength/Deformation |
|---|---|---|---|---|---|---|---|
| 1 | 20 | 10 | | | 35.1 | 0.605 | 58.0 |
| 2 | 20 | 20 | | | 35.2 | 0.594 | 59.3 |
| 3 | 10 | 30 | | | 31.0 | 0.444 | 69.8 |
| 4 | 3 | 40 | | | 24.5 | 0.305 | 78.7 |
| 5 | 20 | 20 | 10 | | 33.2 | 0.575 | 57.7 |
| 6 | 10 | 15 | 15 | | 30.5 | 0.541 | 56.4 |
| 7 | 3 | 20 | 20 | | 23.9 | 0.320 | 74.7 |
| 8 | 20 | 10 | | 20 | 32.8 | 0.625 | 52.5 |
| 9 | 6 | 20 | | 15 | 27.2 | 0.410 | 66.3 |
| 10 | 3 | 20 | | 20 | 22.3 | 0.380 | 58.7 |

*Table 2*

| Comparative examples | Compositions (% by weight) Additive | Amount | Additive | Amount | Strength (Kg) | Deformation (mm) | Ratio of Strength/Deformation |
|---|---|---|---|---|---|---|---|
| 1 | Glass Fiber (1) | 30 | | | 36.1 | 0.777 | 46.5 |
| 2 | Glass Fiber (1) | 10 | | | 31.5 | 1.240 | 25.4 |
| 3 | Glass Fiber (2) | 30 | | | 28.0 | 0.598 | 46.8 |
| 4 | Mica (3) | 40 | | | 25.5 | 0.501 | 50.9 |
| 5 | Glass Bead (4) | 30 | | | 24.6 | 0.501 | 49.1 |
| 6 | Calcium Hydroxide (5) | 50 | | | 24.5 | 0.522 | 46.9 |
| 7 | Wollastonite (6) | 40 | | | 26.8 | 0.525 | 51.0 |
| 8 | Glass Fiber (1) | 15 | Calcium Hydroxide | 25 | 29.0 | 0.824 | 35.2 |
| 9 | Glass Fiber (1) | 30 | Glass Bead | 10 | 34.1 | 0.922 | 37.0 |
| 10 | Glass Fiber (2) | 15 | Calcium Hydroxide | 35 | 14.4 | 0.663 | 21.7 |
| 11 | Mica | 20 | Glass Bead | 20 | 24.5 | 0.515 | 47.6 |

| | | | |
|---|---|---|---|
| Note 1 : | Glass Fiber | (1) | average length of 400 microns, 10 micron diameter |
| Note 2 : | Glass Fiber | (2) | average length of 100 microns, 10 microns diameter |
| Note 3 : | Mica | | crushed product, tens of microns diameter |
| Note 4 : | Glass Bead | | 6 to 66 microns |
| Note 5 : | Calcium Hydroxide | | heavy calcium hydroxide, several microns |
| Note 6 : | Wollastonite | | calcium metasilicate produced in U.S.A. |

WHAT WE CLAIM IS:-

1. A thermoplastic resin composition comprising a thermoplastic resin containing as additives from 1 to 50 percent by weight, based on the total weight of the composition, of a fibrous reinforcing material, and from 5 to 59 percent by weight of a platelet filler, wherein the sum of the said additives does not exceed 60 weight percent of the total composition.
2. A composition as claimed in Claim 1, wherein the said fibrous reinforcing material is glass fibre, carbon fibre, graphite fibre, metal fibres, silicon-carbide fibre, mineral fibres or an organic fibre material.
3. A composition as claimed in Claim 1 or Claim 2, wherein the said platelet filler is mica, glass platelets, sericite, talc, kaolinite, bilofilite or metal foils.
4. A composition as claimed in Claim 1, wherein a particulate additive is incorporated in said composition.
5. A composition as claimed in Claim 4, wherein the said particulate additive is particulate calcium hydroxide, magnesium hydroxide, calcium sulphide, clay, diatomaceous earth, alumina, quartz powder, siliceous sand, glass beads, glass powder, metal powder, antimony trioxide, graphite, organic macromolecules or organic crystalline material.
6. A thermoplastic resin composition as claimed in any of Claims 1 to 5, wherein the said thermoplastic resin is a polyacetal, polybutylene terephthalate, polyethylene terephthalate or a polyamide resin.
7. A thermoplastic resin composition as claimed in Claim 1, substantially as hereinbefore described, with particular reference to the Examples.

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1587894 COMPLETE SPECIFICATION

1 SHEET

*This drawing is a reproduction of the Original on a reduced scale*

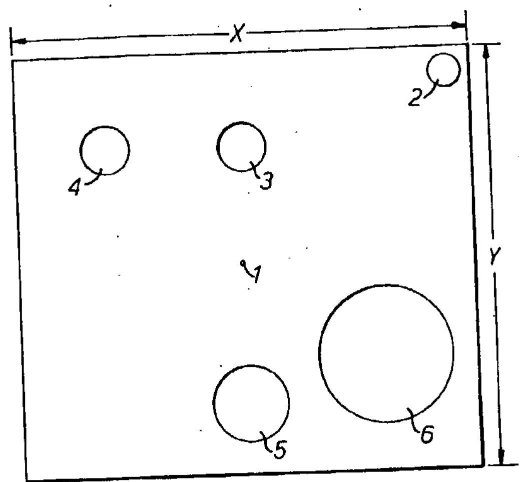


FIG. 1.


FIG. 2.